

W. E. JOHN & KERNICK,
Patent and Trade Mark Agents,
P.O. Box 1840, Pretoria,
(and at P.O. Box 727,
Johannesburg)

REPUBLIC OF SOUTH AFRICA
THE PATENTS ACT, 1952, AS AMENDED

PATENTS FORM No. 1A.
(Convention)

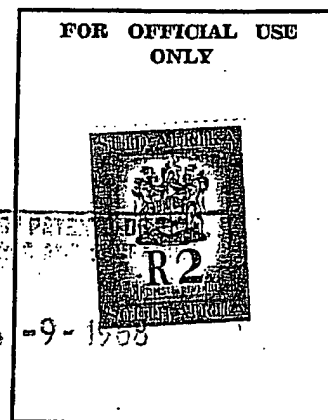
APPLICATION FOR A PATENT UNDER INTERNATIONAL ARRANGEMENTS
(WITH AUTHORISATION OF AGENT)

Filing date and Application No. 68/5954

Full Name(s) of Applicant(s): THE PROCTER & GAMBLE COMPANY.

Address(es) of Applicant(s): 301 East Sixth Street,
Cincinnati, Ohio, U. S. A.

Full Name(s) of Inventor(s): John Joseph Parran, Jr.



I/We do hereby declare that ~~we~~ we are in possession of an invention the title of which is
"ORAL COMPOSITIONS FOR CALCULUS RETARDATION". *Detergent compositions containing particle disposition enhancing agents.*
I/We are the assignee(s) ~~legal representative(s)~~ of the inventor(s) Application(s) for protection
of the invention has/have been made in the following country/countries and on the following official dates
e.g.:-

(country) U. S. A.	(date) 27. 9.67	(No.) 671,117.
(country)	(date)	(No.)
(country)	(date)	(No.)
(country)	(date)	(No.)

The said application or each of the said applications was the first application filed in a convention country in respect of the relevant invention by ~~us~~ us or by any person from whom I/we derive title. To the best of ~~my~~ our knowledge and belief there is no lawful ground for objection to the grant of a patent ~~to us~~ on this application. I/We pray that a patent be granted to ~~us~~ us for the invention in priority over other applicants and that such patent shall have the official date of the first application in a convention country i.e. 27th September, 1967.

I/We hereby appoint the partners and qualified staff of the firm of W. E. JOHN & KERNICK, jointly and severally, to act for me/us in all matters relating to this application and any Letters Patent granted thereon.

Address for Service:
W. E. JOHN & KERNICK,
VAN DER STEL BUILDING,
PRETORIUS STREET,
PRETORIA. (P.O. BOX 1840).

Dated this 16th day of SEPTEMBER 19 68.

Table of Classification	
Class	Sub-class

p.p. THE PROCTER & GAMBLE COMPANY.

W. E. JOHN & KERNICK.
Signature of Applicant(s) and Capacity

PATENTS FORM NO. 3.

16-9-1968



685954

REPUBLIC OF SOUTH AFRICA.

16-9-1968

THE PATENTS ACT, 1952.

COMPLETE SPECIFICATION.

THE PROCTER & GAMBLE COMPANY,
of 301 East Sixth Street,
CINCINNATI, Ohio, U. S. A.

~~"ORAL COMPOSITIONS FOR CALCULUS RETARDATION".~~

*Detergent compositions containing particle disposition
enhancing agents*

We do hereby declare this invention, the manner
in which and the method by which it is to be performed,
to be particularly described and ascertained in and by
the following statement:-

68/5954

THE PROCTER & GAMBLE COMPANY

DETERGENT COMPOSITIONS
CONTAINING PARTICLE DISPOSITION ENHANCING AGENTS

are the assignees of JOHN JOSEPH PARRAN, JR.

THE PROCTER & GAMBLE COMPANY

16th September, 1968,

SEPTEMBER,

TWENTY-SEVENTH
SIXTY-SEVEN.

THIRD

SEPTEMBER, 1969.

G. J. H. SCHOEMAN

APPLICATION FOR A PATENT UNDER INTERNATIONAL ARRANGEMENTS

(WITH AUTHORIZATION OF AGENT)



Filing date and Application No. 16th September, 1968.

68/5954

FOR OFFICIAL USE
ONLY

Full Name(s) of Applicant(s): The Procter & Gamble Company

Address(es) of Applicant(s): 301 East Sixth Street,
Cincinnati, Ohio,
United States of America,

Full Name(s) of Inventor(s): John Joseph Parran, Jr.

I/We do hereby declare that ~~KKM~~/we are in possession of an invention the title of which is

E

"DTERGENT COMPOSITIONS CONTAINING PARTICLE DISPOSITION ENHANCING AGENTS".

~~XXXX~~ I/We are the assignee(s)/~~legal representative(s)~~ of the inventor(s). Application(s) for protection for the invention has/have been made in the following country/countries and on the following official dates i.e.:—

- | | | | | | |
|--------------|------------------|--------|--------------------|-------|---------|
| 1. (country) | United States of | (date) | September 27, 1967 | (No.) | 671,117 |
| 2. (country) | America | (date) | | (No.) | |
| 3. (country) | | (date) | | (No.) | |
| 4. (country) | | (date) | | (No.) | |

The said application or each of the said applications was the first application filed in a convention country in respect of the relevant invention by me/us or by any person from whom I/we derive title. To the best of my/our knowledge and belief there is no lawful ground for objection to the grant of a patent to me/us on this application. I/We pray that a patent be granted to me/us for the invention in priority over other applicants and that such patent shall have the official date of the first application in a convention country i.e. 27th September, 1967.

I/We hereby appoint the partners and qualified staff of the firm of W. E. JOHN & KERNICK, jointly and severally, to act for me/us in all matters relating to this application and any Letters Patent granted thereon.

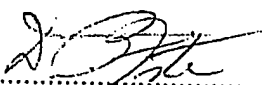
Address for Service:

W. E. JOHN & KERNICK,
VAN DER STEL BUILDING,
PRETORIUS STREET,
PRETORIA (P.O. BOX 1840).

Dated this 20th day of September 19 68

Table of Classification	
Class	Sub-class

THE PROCTER & GAMBLE COMPANY

By 
Signature of Applicant(s) and Capacity

No witnesses or legalization necessary. Vice President

THE PROCTER & GAMBLE COMPANY,
c/o E.E. John & Kernick,
PRETORIA.

W. E. JOHN & KERNICK,
Patent and Trade Mark Agents,
P.O. Box 1840, Pretoria,
(and at P.O. Box 727,
Johannesburg).

1968 SEP 11 11:11
ASSIGNMENT — Required in all cases
where the inventor is not also an
applicant.

REPUBLIC OF SOUTH AFRICA

ASSIGNMENT OF INVENTION

Whereas I/~~we~~ the undersigned John Joseph Parran, Jr.

of 1155 Meredith Drive, Cincinnati, Ohio,
United States of America,

am/~~we~~ the Inventor(~~s~~) of an Invention entitled:—

"DETERGENT COMPOSITIONS CONTAINING PARTICLE DISPOSITION ENHANCING
AGENTS".

and WHEREAS THE PROCTER & GAMBLE COMPANY

~~has~~/have for good and sufficient consideration acquired

said Invention from me/~~us~~ in respect of the Republic of South Africa.

NOW THEREFORE I/~~we~~ hereby assign the said Invention to the said

THE PROCTER & GAMBLE COMPANY

as far as the Republic of South Africa is concerned,

with the right to apply for Letters Patent in ~~his~~/their own name.

DATED this 11th day of September 1968

John Joseph Parran Jr.

Witnesses:

1 *Claudine Spauld*

2 *Steven P. Berman*

Note: No legalization necessary.

PATENTS FORM NO. 3.

REPUBLIC OF SOUTH AFRICA.

THE PATENTS ACT, 1952.

COMPLETE SPECIFICATION.

THE PROCTER & GAMBLE COMPANY,
of 301 East Sixth Street,
CINCINNATI, Ohio, U. S. A.

"ORAL COMPOSITIONS FOR CALCULUS RETARDATION".

We do hereby declare this invention, the manner
in which and the method by which it is to be performed,
to be particularly described and ascertained in and by
the following statement:-

S. Ayala

This invention relates to detergent compositions which have improved capacities to impart residual activity or properties to surfaces washed therewith. It particularly relates to detergent compositions containing water-insoluble or sparingly soluble particulate substances, said composition also containing certain
5 cationic polymers which serve to enhance the deposition and retention of such particulate substances on surfaces washed with the detergent composition.

BACKGROUND OF THE INVENTION

10 The field of this invention is detergent compositions including shampoos (liquid and cream), laundering, hard-surface and dishwashing detergents (granular and liquid), and personal use toilet detergent bars.

Various water insoluble particulate substances have been
15 incorporated in detergent products for the purpose of imparting some residual property or characteristic on surfaces washed with the products. For example, shampoo compositions containing

particulate antidandruff agents have been developed which function by deposition and retention of the particulate agent on the hair and scalp during shampooing. Sufficient quantities of the deposited particulate agents are retained after rinsing to impart some degree of residual antimicrobial activity to the washed hair and scalp. Such antidandruff shampoo compositions are disclosed, for example, by Karsten, Taylor and Parran in U. S. Patent 3,263,733, granted February 22, 1966.

Particulate antimicrobial substances have also been used in various laundry detergents and personal use toilet detergent bars to impart residual antimicrobial activity on the fabrics or skin surfaces washed with same. Such products are disclosed by Reller and Jordan in U. S. Patents 3,134,711, granted May 26, 1964, and 3,256,200, granted June 14, 1966.

Various other water-insoluble or sparingly soluble particulate materials such as sunscreens, fabric brighteners, and whiteners have been employed in detergent compositions and depend for their activity on particle deposition and retention on washed surfaces.

It is apparent that an effective detergent composition, properly used, will by its very nature tend to minimize retention of particulate matter on washed surfaces. Thus, only a relatively small proportion of particles present in such detergent compositions are actually retained after rinsing of the washed surface. Since the activity of antimicrobial and other particulate agents is in part a function of the quantity of particles deposited and retained on the involved surfaces,

measures which enhance deposition and/or promote retention of such particles serve to reduce the quantity of the substance in the composition required to attain a given level of activity or increase the activity attainable with a given concentration of such particles.

SUMMARY OF THE INVENTION

It has now been discovered that certain water-soluble cationic nitrogen-containing polymers having a molecular weight within the range from about 2,000 to about 3,000,000; and having a cationic charge density (as defined hereinafter) greater than .001 in aqueous solution, enhance the deposition and retention of water-insoluble or sparingly soluble particulate substances contained in detergent compositions on surfaces washed therewith.

Although the mechanism whereby this phenomenon occurs is not fully understood, it is believed that the polymer coats or attaches itself in some way on the involved particles imparting a net positive charge thereto which increases the affinity of the particle for the generally negatively charged washed surfaces.

It is therefore an object of this invention to provide detergent compositions which have improved capacities to impart residual activity or properties to surfaces washed therewith.

It is a further object of this invention to provide improved detergent compositions containing water-insoluble or sparingly soluble particulate substances which are deposited and retained on washed surfaces.

It is yet another object of this invention to provide a method for enhancing the deposition of particulate substances from detergent compositions and the retention of such substances on surfaces washed therewith.

5 These and other objects will become apparent from the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The detergent compositions of this invention are comprised of (1) an organic surface active agent (surfactant, i.e.,
10 detergent compound); (2) at least one water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to about 3,000,000 and having a cationic charge density greater than .001 in aqueous solution as hereinafter defined; and (3) a water-insoluble or sparingly soluble
15 particulate substance capable of imparting a desired residual property to a surface to which it becomes affixed.

In its process aspect, this invention is a method for enhancing the deposition and retention of particulate substances upon surfaces washed with a detergent composition containing
20 same, comprising uniformly admixing said particulate substances with a water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to about 3,000,000, and having a cationic charge density greater than .001 in aqueous solution as hereinafter defined
25 and incorporating said mixture in a detergent base.

The "cationic charge density" of a polymer as that term is used herein refers to the ratio of the number of positive charges on a monomeric unit of which the polymer is comprised to the molecular weight of said monomeric unit, i.e.,

5 cationic charge density = $\frac{\text{number of positive charges}}{\text{monomeric unit molecular weight}}$

The cationic charge density multiplied by the polymer molecular weight determines the number of positively charged active sites on a given polymer chain.

Organic surfactants which can be used in the compositions
10 of this invention are anionic, ampholytic, polar nonionic, nonionic, zwitterionic or cationic. The surfactant can comprise from about 2% to about 95% by weight of the total composition. Anionic organic surfactants are generally preferred for the purposes of this invention. Suitable anionic surfactants include
15 the water-soluble salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester radical. Such surfactants include the sodium, potassium, and triethanolamine alkyl sulfates, especially
20 those derived by sulfation of higher alcohols produced by reduction of tallow or coconut oil glycerides; sodium or potassium alkyl benzene sulfonates, especially those of the types described by Gunther et al. in U. S. Patent 2,477,383, granted July 26, 1949, in which the alkyl group contains from about 9 to about 15 carbon
25 atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols obtained from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium salts of sulfuric acid esters of the reaction

product of one mole of a higher alcohol (i.e., tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and the water-soluble salts of condensation products of fatty acids with sarcosine, e.g., triethanolamine N-acyl sarcosinate, the acyl radicals being derived from coconut oil fatty acids.

Preferably, anionic organic surfactants of the high sudsing type are used for the shampoo embodiments of this invention. Thus, alkyl glyceryl ether sulfonates, N-acyl sarcosinates, and alkyl ether ethylene oxide sulfates as described above are used to special advantage. These and the foregoing surfactants can be used in the form of their sodium, potassium or lower alkanolamine (e.g., mono-, di-, and triethanolamine) salts.

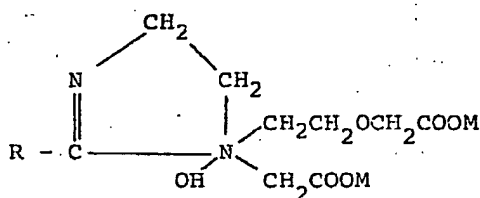
Conventional soaps are also operable anionic surfactants for the purposes of this invention. Suitable soaps include the water-soluble salts, e.g., sodium, potassium, and lower alkanolamine salts of fatty acids occurring in coconut oil, soybean oil, castor oil or tallow, or synthetically produced fatty acids may be used.

Polar nonionic surfactants can be used herein, either alone or in admixture with anionic and/or ampholytic surfactants. Surfactants of this class can serve to enhance lathering and cleaning properties of anionic detergents. By "polar nonionic surfactant" is meant a surfactant in which the hydrophilic group contains a semi-polar bond directly between two atoms, e.g., $N \longrightarrow O$, $P \longrightarrow O$, $As \longrightarrow O$, and $S \longrightarrow O$. (The arrow is the conventional representation of a semi-polar bond.) There is charge separation between the two directly bonded atoms, but the surfactant molecule bears no net charge and does not dissociate into ions.

A preferred polar nonionic surfactant for use in the present compositions is amine oxide of the general formula $R_1R_2R_3N \rightarrow O$, wherein R_1 is an alkyl, alkenyl, or monohydroxyalkyl radical having from about 10 to 16 carbon atoms, and R_2 and R_3 are each methyl, ethyl, propyl, ethanol or propanol radicals. An especially preferred amine oxide is dodecyldimethylamine oxide.

Other operable polar nonionic surfactants are the phosphine oxides having the general formula $R_1R_2R_3P \rightarrow O$, wherein R_1 is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and R_2 and R_3 are each alkyl or monohydroxyalkyl radicals containing from 1 to 3 carbon atoms. A preferred phosphine oxide is dodecyldimethyl phosphine oxide.

Suitable amphoteric surfactants include the alkyl beta-iminodipropionates, $RN(C_2H_4COOM)_2$; alkyl beta-aminopropionates, $RN(H)C_2H_4COOM$; and long chain imidazole derivatives having the general formula:



In each of the above formulae, R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms and M is a cation to neutralize the charge of the anion, e.g., alkali metal such as sodium and potassium and ammonium and substituted ammonium cations. Specific operable amphoteric surfactants include the disodium salt of lauroyl-cycloimidinium-1-ethoxyethionic acid-2-ethionic acid, dodecyl beta-alanine, and the

inner salt of 2-trimethylamino lauric acid. As zwitterionics, the substituted betaines such as alkyl dimethyl ammonio acetates wherein the alkyl radical contains from about 12 to about 18 carbon atoms can also be used. Several examples of this class of zwitterionic surfactants are set forth in Canadian Patent 696,355, granted October 20, 1964.

Especially preferred shampoo compositions in accordance with this invention will contain a non-soap anionic organic surfactant at a concentration of from about 8% to about 30% by weight of the total composition.

Although nonionic and cationic surfactants are not preferred for the purposes of this invention they can nevertheless be used without substantial loss of the advantageous effects of the cationic polymers on deposition and retention of particulate matter on washed surfaces. Nonionic surfactants may be described as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. As those skilled in the art are well aware, the length of the hydrophilic or polyoxyalkylene radical required for condensation with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

For example, a well known class of nonionics is made available on the market under the tradename of "Pluronic". These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide

with propylene glycol. The hydrophobic portion of the molecule, of course, exhibits water insolubility. The molecular weight of this portion is of the order of 950 to 4,000. The addition of polyoxyethylene radicals to this hydrophobic portion tends
5 to increase the water solubility of the molecule as a whole. Liquid products are obtained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Suitable nonionics also include the polyethylene oxide
10 condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having about 6 to 12 carbon atoms, either straight chain or branch chain, in the alkyl group with ethylene oxide in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds
15 may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

Other suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again, a series of
20 compounds may be produced, depending on the desired balance between hydrophobic and hydrophilic elements. For example, compounds (molecular weight from about 5,000 to about 11,000) of about 40% to 80% polyoxyethylene content and resulting from the reaction of ethylene oxide groups with a hydrophobic base

constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

Further satisfactory nonionics include the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, either straight chain or branch chain, with ethylene oxide, an example being a coconut alcohol/ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

Cationic surfactants which can be used in the compositions of this invention include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, coconut alkyl dimethyl benzyl ammonium chloride, dicoconut alkyl dimethyl ammonium chloride, cetyl pyridinium chloride, and cetyl trimethyl ammonium bromide.

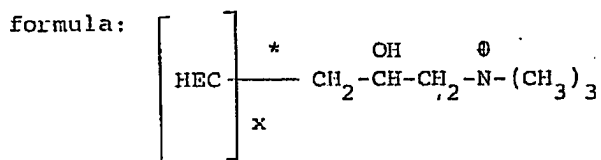
As hereinbefore indicated, the compositions of this invention contain as an essential component a water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to about 3,000,000 and a cationic charge density greater than .001 in aqueous solution.

The water-soluble cationic nitrogen-containing polymers which can be used in the practice of this invention include those in which at least 30 mole percent of the molecular structure is composed of monomeric units containing one or more quaternary ammonium groups and any balance of which is comprised of non-quaternized polymeric units derived from monoethylenically unsaturated monomeric groups. The degree of quaternization must be sufficient to provide a cationic charge density greater than about .001. Such polymers include, for example, quaternized

polyvinylimidazole, quaternized poly(dimethylaminoethylmethacrylate),
 quaternized poly(diethylaminoethylmethacrylate), quaternized
 poly(p-dimethylaminomethylstyrene) and others disclosed by
 Lang in U. S. Patent 3,313,734, granted April 11, 1967, all
 5 having molecular weights within the range from about 2,000 to
 3,000,000.

Still other types of water-soluble cationic polymers use-
 ful herein are the following:

1. Water-soluble quaternary nitrogen-substituted cellulose
 10 ether derivatives, such as the polymer formed by reacting a
 hydroxyethylcellulose (having a degree of substitution with hydroxy-
 ethyl groups of 1.3) with the reaction product of 0.7 moles of
 epichlorohydrin and 0.7 moles of trimethylamine, per substituted
 anhydroglucose unit thereof, said polymer having a cationic charge
 15 density of .002 and a molecular weight within the range from
 about 200,000 to 230,000. This polymer has the structural



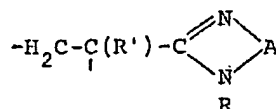
* Hydroxyethylcellulose

- 20 Hydroxyethylcellulose is, of course, comprised of
 hydroxyethyl-substituted anhydroglucose units with varying
 degrees of hydroxyethyl substitution. This material is pre-
 pared by reacting alkaline cellulose with ethylene oxide as
 is more fully described by Gloor et al., Ind. Eng. Chem.,
 25 42:2150 (1950). The extent of substitution with the quaternary
 nitrogen-containing group must be sufficient to provide a cationic
 charge density greater than .001, and the molecular weight of
 the substituted hydroxyethylcellulose polymer must be within the
 range from about 2,000 to 3,000,000.

The preferred cellulose ether derivative from which the quaternary ammonium-substituted polymers described above are prepared include those which are water-soluble nonionic lower alkyl or hydroxyalkyl substituted. Such derivatives include
5 methylcellulose, ethylcellulose, and hydroxyethylcellulose.

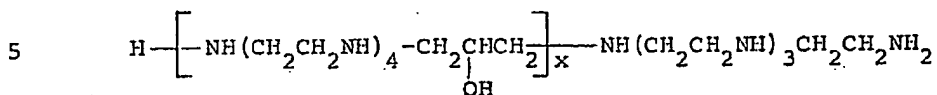
A particularly efficacious quaternary ammonium-substituted cellulose ether derivative for the purpose of this invention is available from Union Carbide under the code name JR-1L. This polymer has a molecular weight within the range from
10 100,000 to 1,000,000 and a cationic charge density of .005.

2. Water-soluble linear polyamines available from The Rohm & Haas Company under the tradename "Primafluc C-3". This polymer has a molecular weight within the range from about 30,000 to 80,000 and a cationic charge density in
15 aqueous solution at pH 7.0 greater than .001, and contains at least 50 mole percent of units of the formula



wherein A is a (C₂-C₃)-alkylene group having at least 2 carbon atoms extending in a chain between the adjoined N atoms,
20 and R and R' are each hydrogen or methyl. This and related polymers operable herein as well as a method for their preparation are fully described in U.S. Patent 3,288,707, granted November 29, 1966.

3. The water-soluble polymers of tetraethylene pentamine and epichlorohydrin commercially available from the Nalco Chemical Company under the tradenames Nalco 600 and Nalcolyte 605. Such polymers have the formula:



wherein x is an integer of sufficient magnitude to yield a polymer having a viscosity at 74°F of 21 to 42 centipoise. These polymers have a molecular weight within the range from about 2,000 to 3,000,000 and a cationic charge density greater
10 than .001 in aqueous solution at pH 7.0.

4. Coagulant Aid #225 commercially available from The Calgon Company. This product is a water-soluble nitrogen-containing polymer having a molecular weight within the range from about 30,000 to 3,000,000 and a cationic charge density greater
15 than .001 in aqueous solution at pH 7.0.

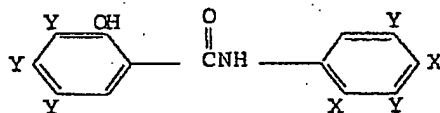
5. Conductive Polymer #261 commercially available from The Calgon Company. This product is a water-soluble nitrogen-containing polymer having a molecular weight within the range from about 30,000 to 3,000,000 and a cationic charge density
20 greater than .001 in aqueous solution at pH 7.0.

If the molecular weight of the cationic polymers employed herein is less than about 2,000, no substantial enhancement of particle deposition occurs. Best results are obtained with polymers having a molecular weight within the range from about
25 30,000 to about 1,000,000.

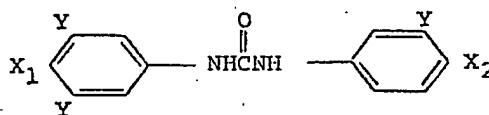
The cationic polymer can be employed herein at a concentration within the range from about 0.1% to about 10.0% by weight, preferably from about 0.25% to about 4.0% by weight.

Particulate substances which can be used in the detergent compositions of this invention preferably have an average particle diameter within the range from about 0.2 to about 50 microns and include water-insoluble or sparingly soluble antimicrobial agents, sunscreens, fabric brighteners, and various substances which create a favorable skin feel after washing. These particulate substances depend on deposition and retention on washed surfaces to produce their intended effect.

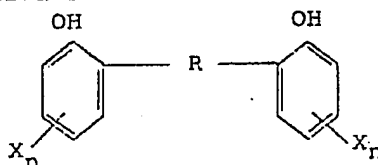
Particulate antimicrobial substances, the deposition and retention of which is enhanced by the cationic polymers described herein include, for example, (a) substituted salicylanilides having the general formula:



wherein X is hydrogen or halogen, and Y is hydrogen, halogen or trifluoromethyl; (b) substituted carbanilides having the general structural formula:



wherein Y is hydrogen, halogen, or trifluoromethyl, X₁ is halogen or ethoxy, X₂ is hydrogen or halogen; (c) substituted bisphenols having the general structural formula:



wherein X is a halogen and n is an integer from 1 to 3, R is an alkylene radical having from 1 to 4 carbon atoms or divalent sulfur; and (d) mixtures of (a), (b), and (c).

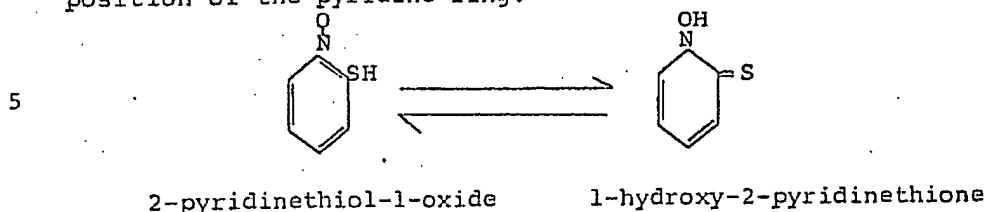
The salicylanilides encompassed by (a) above include
5 3,4',5-tribromosalicylanilide; 5-bromosalicyl-3,5-di(trifluoromethyl)anilide; 5-chlorosalicyl-3,5-di(trifluoromethyl)anilide; 3,5-dichlorosalicyl-3,4-dichloroanilide; and 5-chlorosalicyl-3-trifluoromethyl-4-chloroanilide. These and other salicylanilides useful herein are disclosed by Bindler and Model in U.S. Patent
10 2,703,332, granted March 1, 1955.

The preferred carbanilides of (b) above include 3,4,4'-trichlorocarbanilide; 3-trifluoromethyl-4,4'-dichlorocarbanilide; 3-trifluoromethyl-3',4,4'-trichlorocarbanilide; 3,3'-bis(trifluoromethyl-4-ethoxy-4'-chlorocarbanilide; and 3,5-bis(tri-
15 fluoromethyl)-4-chlorocarbanilide.

The compounds in (c) above in which R represents an alkylene radical are more fully described in U.S. Letters Patent 2,555,077, granted December 26, 1950. The preferred compounds of the general class of (c) above are those which are symmetrical in
20 structural configuration, such as bis(5-chloro-2-hydroxyphenyl)methane, bis(3,5-dichloro-2-hydroxyphenyl)methane, bis(3,5,6-trichloro-2-hydroxyphenyl)methane, bis(3,5-dichloro-2-hydroxyphenyl)sulfide, bis(3,5,6-trichloro-2-hydroxyphenyl)sulfide, and mixtures thereof.

25 Additional antimicrobial compounds suitable for use in this invention are N-trichloromethylmercapto-4-cyclohexene-1,2-dicarboximide and N-(1,1,2,2-tetrachloroethylsulfenyl)-cis-Δ-4-cyclohexene-1,2-dicarboximide.

Preferred antibacterial agents employed herein are salts of 2-pyridinethiol-1-oxide which has the following structural formula in tautomeric form, the sulfur being attached to the number 2 position of the pyridine ring:



Heavy metal salts of the above compounds are sparingly soluble and have a high degree of antibacterial activity.

Preferred salts include zinc, cadmium, tin and zirconium 2-pyridinethiol-1-oxide.

Combinations of the above-described antibacterial substances can also be used to advantage. Such combinations are illustrated in U.S. Patent 3,281,366, granted October 25, 1966.

These antimicrobial compounds are used in particulate form, with average particle sizes ranging from about 0.2 to about 30 microns. The quantity of antimicrobial agent employed can range from about 0.1% to about 10% and preferably from about 0.5% to about 2.0% by weight.

Preferred antimicrobial detergent compositions in accordance with this invention especially adapted to washing hair and scalp are comprised of from about 10% to about 35% by weight of at least one non-soap anionic, polar nonionic, ampholytic or zwitterionic surfactant; from about 0.25% to about 2.0% by weight of a water-soluble cationic nitrogen-containing polymer having a cationic charge density greater than about .001 and having an average molecular weight within the range from about 30,000 to about 1,000,000; from about 0.5% to about 2.0% by weight of a

water-soluble or sparingly soluble antimicrobial substance in particulate form; and the balance substantially water.

Detergent compositions in accordance with this invention can be prepared by methods well known in the art; however, as
5 hereinbefore indicated, it has been found that especially good results are obtained when the cationic polymer and particulate substances are uniformly admixed in an initial step, with the mixture then being added to an aqueous solution or slurry of the surfactant. If the polymeric component and particulate substance
10 are added to the surfactant separately, the degree of deposition and retention enhancement effected by the polymer will be somewhat less.

Each of the aforementioned components can be incorporated in an aqueous vehicle which may, in addition, include such materials
15 as organic solvents, such as ethanol; thickeners, such as carboxymethylcellulose, magnesium-aluminum silicate, hydroxy-ethylcellulose or methylcellulose; perfumes; sequestering agents, such as tetrasodium ethylenediaminetetraacetate; and opacifiers, such as zinc stearate or magnesium stearate, which are useful in
20 enhancing the appearance or cosmetic properties of the product.

Coconut acyl mono- or diethanol amides as suds boosters, and strongly ionizing salts such as sodium chloride and sodium sulfate may be used to advantage.

Toilet detergent or soap bars containing a cationic polymer
25 and particulate substance according to this invention can be based on soap or non-soap synthetic detergents and can also contain a variety of adjuvants to improve product performance or appearance. Examples of such adjuvants include free fatty acids or cold cream to improve cosmetic properties, perfumes, inorganic salts to
30 improve bar firmness, insoluble soap to improve bar texture, coloring matter and the like.

In the case of heavy-duty laundering detergents containing the cationic polymers and particulate substances in accordance with this invention, such detergents can be in granular, flake, liquid or tablet form and can contain, in addition to detergent
5 and inorganic or organic builder compounds (such as those disclosed by Diehl in U.S. Patent 3,159,581, granted December 1, 1964), minor amounts of adjuvant materials which make the product more effective or more attractive. The following are mentioned by way of example. A tarnish inhibitor such as
10 benzotriazole or ethylenethiourea may also be added in amounts up to about 2%. Fluorescers, perfume and color while not essential in the compositions of the invention, can be added in amounts up to about 1%. An alkaline material or alkali, such as sodium hydroxide or potassium hydroxide, can be added in minor
15 amounts as supplementary pH adjusters when needed. There can also be mentioned as suitable additives, brightening agents, sodium sulfate, and sodium carbonate.

Corrosion inhibitors generally are also added. Soluble silicates are highly effective inhibitors and can be added to
20 certain formulas of this invention at levels of from about 3% to about 8%. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of $\text{SiO}_2:\text{M}_2\text{O}$ of from 1.0:1 to 2.8:1 can advantageously be used. M in this ratio refers to sodium or potassium. A sodium silicate having a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$
25 of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotropic agent at times is found desirable. Suitable hydrotropes are water-soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. The preferred hydrotropes are the potassium or sodium toluenesulfonates. The hydrotrope salt can be added, if desired, at levels of 1% to about 12%. While a hydrotrope will not ordinarily be found necessary, it can be added if so desired, for any reason including the preparation of a product which retains its homogeneity at a low temperature.

The term "coconut alkyl" as used herein and in the following examples refers to alkyl groups which are derived from the middle cut of coconut alcohol having the following approximate chain length distribution: 2%-C₁₀, 66%-C₁₂, 23%-C₁₄, and 9%-C₁₆. Other compounds designated as coconut oil derived are based on unfractionated coconut oil or its fatty acids.

The following examples are illustrative of several detergent compositions of this invention.

EXAMPLE I

A shampoo composition is prepared having the following composition:

Parts by Weight

5	Sodium coconut alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl)	25.0
10	Sodium tallow alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl; the tallow alkyls correspond to those of substantially saturated tallow alcohols and contain approximately 2% C ₁₄ , 32% C ₁₆ and 66% C ₁₈)	3.0
	Sodium chloride	6.7
	Sodium sulfate	3.3
15	Sodium N-lauroyl sarcosinate	3.8
	N-coconut acyl sarcosine	1.2
	Diethanolamide of coconut fatty acids	2.0
	Acetylated lanolin	1.0
	Perfume	0.4
20	Color	0.04
	Zinc 2-pyridinethiol-1-oxide*	2.0
	JR-1L**	0.5
	Water	Balance
25	* Average particle size 2 microns ** Quaternary ammonium-substituted cellulose ether derivative having a molecular weight from 100,000 to 1,000,000 and a cationic charge density of .005, as hereinbefore defined.	

The zinc pyridinethione and JR-1L are uniformly admixed and added to and uniformly mixed with the balance of the components. The resulting product is a stable cream having excellent cosmetic and antidandruff properties. The degree of deposition of zinc pyridinethione from this composition is much greater than the degree of deposition attained with a similarly formulated product which contained no cationic polymer.

Residual antimicrobial activity of surfaces washed with this composition is markedly greater as compared to surfaces washed with a control product without polymer.

Compositions identical to the composition of Example I, but containing 5 micron diameter particles of 3,4,4'-trichloro-carbanilide; 3,4',5-tribromosalicylanilide; 4,4'-dichloro-3-(trifluoromethyl)carbanilide; and bis(2-hydroxy-3,5,6-trichlorophenyl)methane, and 6.5 micron particles of N-trichloromethyl-mercapto-4-cyclohexene-1,2-dicarboximide and N-(1,1,2,2-tetrachlorethylsulfenyl)-cis-Δ-4-cyclohexene-1,2-dicarboximide, respectively, in place of zinc 2-pyridinethiol-1-oxide are prepared and compared with control compositions containing these same compounds without cationic polymer. The degree of deposition and retention of these compounds in the presence of the cationic polymer is found to be substantially greater than is attached with the control compositions, and a corresponding increase in residual antimicrobial activity is observed on surfaces washed therewith.

EXAMPLE II

Another antimicrobial detergent formulation in accordance with this invention is formulated as follows:

	<u>Parts by Weight</u>
Triethanolamine coconut alkyl sulfate	10.0
25 Coconut alkyl dimethyl amine oxide	10.0
Monoethanol amide of coconut fatty acids	5.0
Ethanol	10.0
Water-soluble cationic polymer*	0.75
30 Cadmium 2-pyridinethiol-1-oxide (Average particle size 3.0 microns)	0.25

Water, NaOH to adjust to pH 8.5

Balance

5 * Quaternary nitrogen-substituted cellulose derivative formed by reacting a hydroxyethylcellulose, having a degree of substitution with hydroxyethyl groups of 1.3, with the reaction product of 0.7 moles of epichlorohydrin and 0.7 moles of trimethylamine, per substituted anhydroglucose unit thereof, said polymer having a molecular weight of 200,000-230,000 and a cationic charge density of .002.

10 This composition has excellent antimicrobial properties and in usage imparts sustained antimicrobial activity to surfaces washed therewith. The amine oxide can be replaced, in whole or in part, with coconut beta-iminodipropionate, disodium; lauroylcycloimidinium-1-ethoxy ethionic acid-2-ethionic
15 acid, disodium; or dodecyl ammonioacetate, with substantially equivalent results.

Further compositions in accordance with this invention are as follows.

EXAMPLE III

20 A liquid detergent composition suitable for use as an antidandruff shampoo is formulated as follows:

		<u>Parts by Weight</u>
	Triethanolamine coconut alkyl sulfate	20.0
	Monoethanol amide of coconut fatty acid	4.5
25	Magnesium aluminum silicate	0.9
	Methylcellulose	0.23
	Dye	0.008
	Perfume	0.8
	Zinc 2-pyridinethiol-1-oxide*	1.0
30	Primaflor C-3**	0.5
	Water	Balance

* Average particle size 1.5 microns

** Water-soluble linear polyamine having a molecular weight of 30,000-80,000 and a cationic charge density in aqueous
35 solution at pH 7.0 greater than .001, as hereinbefore defined.

This composition provides a substantial degree of anti-dandruff effect when used in the customary fashion. The degree of deposition and retention of particulate zinc pyridinethione on the hair and scalp after shampooing with this product is substantially greater than is attained with a similar composition without the polyethylenimine/ethylene oxide reaction product.

Additional detergent compositions in accordance with this invention are formulated as follows:

		EXAMPLES							
		<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>	<u>IX</u>	<u>X</u>	<u>XI</u>
10	Sodium coconut alkyl (ethoxy) ₃ sulfate	20				7.5			
15	Sodium lauroyl sarcosinate		25	5	10				
	Sodium dodecyl benzene sulfonate			10					25
	2-trimethylamine lauric acid			5	5		25		
20	Triethanolamine coconut alkyl monoglyceride sulfonate					7.5			
25	Potassium coconut soap				5			20	
	Ethanol					10.0			5.0
	Nalco 600*	2.0		2.5			0.5		1.0
	Coagulant Aid 225*		1.5		2.5	0.5		2.0	
30	Tin 2-pyridine-thiol-1-oxide (average particle size 7 microns)	1.0		0.5		2.0		0.1	
	Zirconium 2-pyridinethiol-1-oxide (average particle size 4 microns)		1.0		0.5		2.5		1.5
35	Water								Balance

* As hereinbefore defined

Each of the above compositions impart a residual antimicrobial activity to surfaces washed therein which is substantially greater than is attainable with similar compositions without the polymeric component.

5 In Example XI, distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, or dicoconut alkyl dimethyl ammonium chloride can be used in place of sodium dodecyl benzene sulfonate without loss of the improved deposition and retention of zirconium 2-pyridinethiol-1-oxide
10 particles effected by the polyethylenimine.

In Example IV, sodium coconut alkyl (ethoxy)₃ sulfate can be replaced with the condensation product of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol and having a molecular weight of 1600
15 or the condensation product of octyl phenol and ethylene oxide using a mole ratio of 1:15, with substantially equivalent results.

EXAMPLE XII

An antimicrobial milled toilet detergent bar which also constitutes a preferred embodiment of this invention is prepared
20 in accordance with methods well known in the art and having the following composition:

	<u>Parts by Weight</u>
Sodium alkyl glyceryl ether sulfonate*	8.0
Potassium alkyl sulfate*	20.0
25 Magnesium soap of 80:20 tallow: coconut fatty acids	16.7
Sodium soap of 80:20 tallow: coconut fatty acids	32.4
30 Inorganic salts (sodium and potassium chlorides and sulfates)	9.2
3,4',5-tribromosalicylanilide (Average particle size 5 microns)	1.0
Cationic polymer**	2.0
Water and miscellaneous	10.7

* Alkyl groups derived from middle cut of alcohols obtained by catalytic reduction of coconut alcohol which has a chain length distribution substantially as follows: 2%-C₁₀, 66%-C₁₂, 23%-C₁₄, and 9%-C₁₆.

5 ** Quaternary ammonium-substituted hydroxyethylcellulose ether formed by reacting a hydroxyethylcellulose ether (having a degree of substitution with hydroxyethyl groups of 1.3) with the reaction product of 0.7 moles epichlorohydrin and 0.7 moles of trimethylamine per substituted anhydroglucose
10 unit thereof, said polymer having a cationic charge density of .002 and a molecular weight within the range from about 200,000 to 230,000.

The deposition and retention of the particulate antimicrobial agent 3,4',5-tribromosalicylanilide upon skin washed with
15 the above composition is substantially greater than occurs with a control composition without cationic polymer.

Toilet detergent bars identical in composition to the bar described above are prepared, replacing the 3,4',5-tribromosalicylanilide with 4 micron particles of the antimicrobial
20 agents 3,4,4'-trichlorocarbanilide; 4,4'-dichloro-3-(trifluoromethyl) carbanilide; bis(2-hydroxy-3,5,6-trichlorophenyl) methane; and a 1:1 mixture of 4,4'-dichloro-3-(trifluoromethyl) carbanilide and 3,4',5-tribromosalicylanilide, respectively, with improved deposition and retention of the antimicrobial
25 particles being attained in each case relative to control compositions without cationic polymer.

Additional toilet detergent bars are prepared as in Example XII each containing one of the following cationic polymers in place of the quaternary ammonium-substituted cellulose ether
30 polymer employed therein:

- (1) Nalcolyte 605, as hereinbefore defined.
- (2) Coagulant Aid 225, as hereinbefore defined.
- (3) Conductive Polymer 261, as hereinbefore defined.

- (4) Polyvinylimidazole substantially completely quaternized with dimethyl sulfate, having a molecular weight of 5,000, and a cationic charge density of .009.
- 5 (5) Poly(dimethylaminoethylmethacrylate) substantially completely quaternized with methyl phosphate, having a molecular weight of 1,000,000, and a cationic charge density of .006.
- 10 (6) Poly(diethylaminoethylmethacrylate) substantially completely quaternized with dimethyl sulfate, having a molecular weight of 300,000, and a cationic charge density of .005.

Each of these toilet detergent bars provides a degree of 3,4',5-tribromosalicylanilide particle deposition and retention on skin washed therewith which is substantially greater than is attained with toilet detergent control bars without such polymers.

EXAMPLE XIII

An antimicrobial granular built laundry detergent product is prepared by conventional means, having the following composition:

	<u>Parts by Weight</u>
25 Sodium alkyl benzene sulfonate (the alkyl group averaging about 12 carbon atoms and being derived from polypropylene)	17.5
Sodium tripolyphosphate	49.7
Sodium sulfate	13.3
Silicate solids	7.0
30 3,4,4'-trichlorocarbanilide (particle size averaging 3 microns)	0.5
Quaternized polyvinylimidazole*	1.5

* Polyvinylimidazole in which 80% of the vinylimidazole units are quaternized with dimethyl sulfate, having a molecular weight of 250,000 and a cationic charge density of .007.

Fabrics laundered in this product retain a substantially greater quantity of 3,4,4'-trichlorocarbanilide particles than do fabrics washed in a control product formulated as above, but without the cationic polymer.

5 Each of the foregoing Examples describe embodiments of this invention which involve antimicrobial particulate substances. As hereinbefore disclosed, the deposition and retention of other particulate substances are also enhanced by the cationic polymers. The following examples are illustrative of detergent composi-
10 tions in accordance with this invention containing representative particulate substances which function through deposition and retention on washed surfaces.

Toilet detergent bars desirably contain a sunscreen or ultraviolet absorber which will deposit on the skin in the
15 course of washing therewith to provide protection against harmful sun rays. Suitable particulate ultraviolet absorbers which can be incorporated in detergent bars for this purpose include, for example, 2-hydroxy-4-n-octoxybenzophenone, 2-hydroxy-4-methoxy-2-carboxybenzophenone, and 2-hydroxy-4-
20 methoxybenzophenone. These materials are insoluble particulate solids which are employed in bar soap formulations in concentrations ranging from about 1% to about 5% by weight.

EXAMPLE XIV

A toilet soap bar containing an ultraviolet absorber is
25 formulated in accordance with this invention as follows:

		<u>Percent By Weight</u>
	Sodium soap of 50:50 tallow:coconut fatty acids	73.19
	Coconut fatty acid	7.30
5	Cold cream	1.10
	Inorganic salts (sodium chloride and sulfate and silicate solids)	0.87
	Perfume	1.23
	2-Hydroxy-4-n-octoxybenzophenone (Particle size 10 microns)	2.50
10	Cationic polymer*	3.00
	Miscellaneous	0.81
	Water	10.00

* Same as Example XII

15 When used in the customary fashion, the toilet soap bar of this Example effects a substantially greater degree of deposition and retention of the particulate ultraviolet absorber (2-hydroxy-4-n-octoxybenzophenone) on the washed skin surfaces than does an identical composition without polymer.

20 Additional toilet soap bars are prepared as above but containing 2-hydroxy-4-methoxy-2'-carboxybenzophenone and 2-hydroxy-4-methoxybenzophenone, respectively, in place of 2-hydroxy-4-n-octoxybenzophenone, with substantially equivalent results.

Toilet soap bars formulated in accordance with Example XIV are prepared containing polyvinylimidazole substantially completely quaternized with dimethyl sulfate, having a molecular weight of 200,000 and a cationic charge density of .009; 5 quaternized poly(p-dimethylaminomethylstyrene) having a molecular weight of 250,000 and a cationic charge density of .006; and JR-1L, a quaternary ammonium-substituted cellulose derivative supplied by Union Carbide, having a molecular weight within the range from 100,000 to 1,000,000, and a cationic charge density 10 of .004; respectively, in place of the cationic polymer employed in that Example. The resulting products are substantially equivalent to the product of Example XIV in terms of particle deposition and retention.

Other insoluble particulate substances which are desirably 15 incorporated in toilet soap or detergent bars include the so-called "skin feel enhancers". Such materials are deposited as particles on the skin in the course of washing and create a favorable skin "feel" after washing. Such materials include, for example, nicotinic acid, talc and silicones, such as Dow-Corning Silicone 20 F-157. These materials are desirably incorporated in a toilet bar formula at levels of about 10% by weight.

EXAMPLE XV

A bar soap formulation as set forth in Example XIV is prepared substituting 10.2% by weight of nicotinic acid particles 25 (average particle size 5 microns) for the 2-hydroxy-4-n-octoxy-benzophenone and coconut fatty acid. The resulting composition yields a substantially greater degree of deposition and retention of

nicotinic acid particles on skin washed with the bar than is attained with a bar similarly formulated but without cationic polymer. Similar results are obtained when Dow-Corning Silicone F-157 is used in place of nicotinic acid.

Various insoluble fabric whiteners or brighteners, such as fluorescent dyes and bluing, e.g., ultramarine blue, deposit as particles on fabrics washed with laundry detergent products containing same. Such materials can be used in heavy-duty laundry detergent products in concentrations up to about 1% by weight.

EXAMPLE XVI

A built liquid detergent formulation containing a particulate bluing material and a cationic polymer in accordance with this invention is formulated as follows:

		<u>Percent by Weight</u>
	3(N,N-dimethyl-N-coconutammonio)-2-hydroxypropane-1-sulfonate	9.00
20	Tergitol 12-P-12 (condensation product of 12 moles of ethylene oxide and one mole of dodecylphenol)	3.00
	Tripotassium methylene diphosphonate	26.00
	Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 1.6:1$)	3.00
	Potassium toluenesulfonate	8.50
25	Sodium carboxymethylhydroxyethylcellulose	0.30
	Ultramarine blue (particle size 1.8 microns)	0.15
	Cationic polymer*	3.5
	Water	Balance
30	* Poly(diethylaminoethylmethacrylate) substantially completely quaternized with dimethyl sulfate, having a molecular weight within the range from about 1,000 and 5,000,000 and a cationic charge density of .005.	

The above composition when used to launder white fabrics in the conventional method results in the deposition and retention of substantially greater quantities of the ultramarine blue particles on the washed fabrics than occurs when a product similarly formulated but without cationic polymer is used.

Several additional detergent compositions exemplifying the invention are prepared as follows:

Parts by Weight				
	<u>Example</u>	<u>XVII</u>	<u>XVIII</u>	<u>XIX</u>
10	Sodium coconut alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl)	25.0	25.0	25.0
15	Sodium tallow alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl; the tallow			
20	alkyls correspond to those of substantially saturated tallow alcohols and contain approximately 2%-C ₁₄ , 32%-C ₁₆ , and 66%-C ₁₈)	3.0	3.0	3.0
25	Sodium chloride	6.7	6.7	6.7
	Sodium sulfate	3.3	3.3	3.3
	Sodium N-lauroyl sarcosinate	3.8	3.8	3.8
	N-coconut acyl sarcosine	1.2	1.2	1.2
30	Diethanolamide of coconut fatty acids	2.0	2.0	2.0
	Acetylated lanolin	1.0	1.0	1.0
	N-Trichloromethylmercapto-4-cyclohexene-1,2-dicarboximide*	0.5	1.0	
	N-(1,1,2,2-tetrachloroethylsulfenyl)-cis-4-cyclohexene-1,2-dicarboximide**			1.0

	<u>XVII</u>	<u>XVIII</u>	<u>XIX</u>
Polymer (1)	1.0		
Polymer (2)		2.5	
Polymer (3)			4.0
5 Water	- - - - -	Balance	- - - - -

* Average particle size 6.5 microns

** Average particle size 10.0 microns

10 Polymer (1) in the above Example is poly(diethylaminoethyl-methacrylate) substantially completely quaternized with dimethyl-sulfate, having a molecular weight of 2,000,000 and a cationic charge density of .005.

Polymer (2) is JR-1L.

Polymer (3) is Primaflor C-3.

Each of the above compositions provides a substantially
15 greater degree of deposition and retention of the particulate antimicrobial agents contained therein than similar compositions formulated without these polymers.

The degree of enhancement of particle deposition and retention in the presence of cationic polymer is demonstrated by the
20 Slide Particle Deposition test conducted as follows:

Dandruff scales are collected from the scalps of afflicted individuals and mounted on glass slides with a clear acrylic adhesive. The dandruff slides are covered with a clean white polyester/cotton cloth, wetted with water, and washed with a test
25 detergent composition by brushing the cloth-covered slide with a soft toothbrush and using 20 grams of the detergent composition for 50 strokes. The slides are then rinsed for one minute with cloth in place and then for two minutes with cloth removed. The rinse water used is tap water at 37°C with a flow rate of
30 4 liters per minute. The slides are then allowed to dry.

The washed slides are examined microscopically at 400 diameters magnification using cross polarized filters. Deposition is graded on a 0-4 scale, no deposition being given a 0 grade, while maximum expected deposition is given a 4 grade. Grades in between vary approximately linearly with the density of deposited particles. Several areas of each slide are given whole number grades before the average for that slide is taken to the nearest 1/4 of a deposition grade. In each test three slides for each test material are treated in random order. All grading and washing is done on a blind basis.

Detergent compositions substantially corresponding to the composition of Example I but containing 0.5% by weight of zinc 2-pyridinethiol-1-oxide and 2.0% by weight of various cationic polymers of this invention were tested against a control composition without polymer using the method described above. The following results were obtained.

	<u>Polymer</u>	<u>Deposition</u>		<u>Improvement of Deposition Grade</u>
		<u>Test</u>	<u>Control</u>	
20	Nalcolyte 605	3.08	2.00	1.08
	Primafluc C-3	3.08	2.00	1.08
	Coagulant Aid 225	3.08	2.00	1.08
	Conductive Polymer 261	3.08	1.75	1.33
25	JR-1L	3.08	2.00	1.08
	PVI ⁽¹⁾	3.00	2.00	1.00
	DMAEMA ⁽²⁾	2.42	1.75	0.67
	DEAEMA ⁽³⁾	2.50	1.75	0.75
30	⁽¹⁾ Polyvinylimidazole substantially completely quaternized with dimethyl sulfate, having a molecular weight of from 5 to 20 x 10 ⁵ , and a cationic charge density of .009.			
	⁽²⁾ Poly(dimethylaminoethylmethacrylate) substantially completely quaternized with methyl phosphate, having a molecular weight between 1,000 and 5,000,000 and a cationic charge density of .006.			

(3) Poly(diethylaminoethylmethacrylate) substantially completely quaternized with dimethyl sulfate, having a molecular weight within the range from about 1,000 and 5,000,000 and a cationic charge density of .005.

5 It can be seen that substantial enhancement of particle deposition and retention is effected by the inclusion of representative cationic polymers in detergent formulations containing same.

 It will be obvious to those skilled in the art that
10 the concept of this invention is applicable to a wide variety of insoluble or sparingly soluble particulate substances in addition to those specifically described in the foregoing specification. For example, perfumes which have been adsorbed on insoluble particulate resinous substances can be
15 deposited on skin, fabrics and other surfaces washed with detergent compositions containing same to a substantially greater degree, through the inclusion in said compositions of a cationic polymer as herein defined.

What is claimed is:

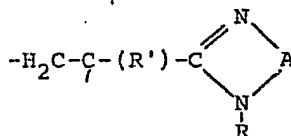
HAVING NOW in detail described and ascertained our said invention and the manner in which it is to be performed, we declare that what we claim is:-

1. " A detergent composition comprising (1) an organic surfactant; (2) a water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to 3,000,000 and a cationic charge density greater than about .001, said polymer being selected from the group consisting of:

(a) quaternary ammonium-substituted cellulose ether derivatives;

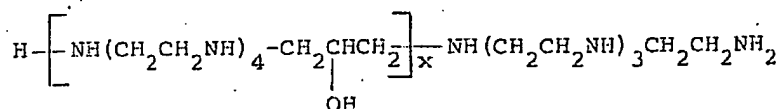
(b) polymers at least 30 mole percent of the molecular structure of which is composed of quaternized vinyl-imidazole, quaternized diethylaminoethylmethacrylate, quaternized dimethylaminoethylmethacrylate, quaternized p-dimethylaminomethylstyrene monomeric units, or combinations thereof,

(c) linear polyamines at least 50 mole percent of the molecular structure of which is composed of monomeric units of the structure



wherein A is a (C₂-C₃) alkylene group having at least two carbon atoms extending in a chain between the adjoined N atoms, and R and R' are each hydrogen or methyl,

(d) polymers of tetraethylenepentamine and epichlorohydrin having the structure



wherein x is an integer of sufficient magnitude to yield a polymer having a viscosity at 74°F of 21 to 42 centipoise,

(e) Coagulant Aid #225, and

30 (f) Conductive Polymer #261;

and (3) a water-insoluble or sparingly soluble particulate substance capable of imparting a desired residual property to a surface to which it becomes affixed.

2. The composition of Claim 1 wherein the cationic polymer is a quaternary ammonium-substituted cellulose ether derivative formed by reacting a hydroxyethylcellulose ether having a degree of substitution with hydroxyethyl groups of 1.3 with the reaction
5 product of 0.7 moles of epichlorohydrin and 0.7 moles of trimethylamine per substituted anhydroglucose unit thereof.

3. The composition of Claim 1 wherein the polymer is a substantially completely quaternized polyvinylimidazole.

4. The composition of Claim 1 wherein the polymer is a substantially completely quaternized poly(diethylaminoethylmethacrylate).

5. The composition of Claim 1 wherein the polymer is a substantially completely quaternized poly(dimethylaminoethylmethacrylate).

6. The composition of Claim 1 wherein the polymer is a substantially completely quaternized poly(p-dimethylaminomethylstyrene).

7. The composition of Claim 1 wherein the polymer is a copolymer of equimolar quantities of vinylbenzyltrimethylammonium chloride and acrylamide.

8. The composition of Claim 1 wherein the particulate substance is a heavy metal salt of 2-pyridinethiol-1-oxide.

9. The composition of Claim 1 wherein the particulate substance is 3,4,4-trichlorocarbanilide.

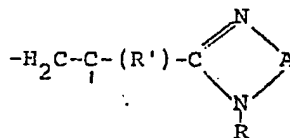
10. The composition of Claim 1 wherein the particulate substance is 3,4',5-tribromosalicylanilide.

11. The composition of Claim 1 wherein the particulate substance is 4,4'-dichloro-3-(trifluoromethyl)carbanilide.

12. The composition of Claim 1 wherein the particulate substance is bis(2-hydroxy-3,5,6-trichlorophenyl)methane.

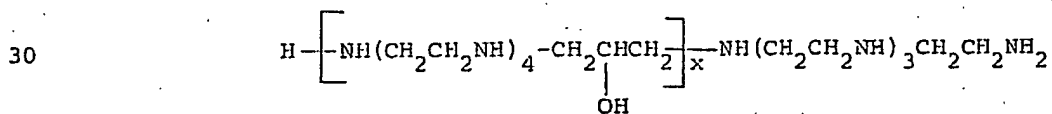
13. A detergent composition comprising (1) from about 2% to about 95% of a water-soluble salt of a member selected from the group consisting of higher fatty acids, anionic organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a sulfuric or sulfonic acid ester radical and acyl sarcosinates, wherein the acyl group contains from about 10 to about 18 carbon atoms; (2) from about 0.25% to about 4.0% of a water-soluble cationic polymer having a molecular weight within the range from about 2,000 to about 3,000,000, and a cationic charge density greater than .001, said polymer being selected from the group consisting of

- (a) quaternary ammonium-substituted cellulose derivatives,
- (b) polymers at least 30 mole percent of the molecular structure of which is composed of quaternized vinyl-imidazole, quaternized diethylaminoethylmethacrylate, quaternized dimethylaminoethylmethacrylate, quaternized p-dimethylaminomethylstyrene monomeric units, or combinations thereof,
- (c) linear polyamines at least 50 mole percent of the molecular structure of which is composed of monomeric units of the structure



wherein A is a (C₂-C₃) alkylene group having at
 25 least two carbon atoms extending in a chain between
 the adjoined N atoms, and R and R' are each hydrogen
 or methyl,

(d) polymers of tetraethylenepentamine and epichlorohydrin
 having the structure



wherein x is an integer of sufficient magnitude to
 yield a polymer having a viscosity at 74°F of 21 to
 42 centipoise,

(e) Coagulant Aid #225, and

35 (f) Conductive Polymer #261;

and (3) from about 0.1% to about 10.0% of a water-insoluble or
 sparingly soluble particulate substance capable of imparting
 a desired property to surfaces to which it becomes affixed,
 said particles having an average diameter within the range from
 40 0.2 to 30 microns.

14. The composition of Claim 13 wherein the particulate sub-
 stance is an antimicrobial agent selected from the group
 consisting of zinc 2-pyridinethiol-1-oxide, 3,4,4'-trichlorocar-
 banilide, 3,4',5-tribromosalicylanilide, 4',4'-dichloro-3-(tri-
 5 fluoromethyl)carbanilide, bis-(2-hydroxy-3,5,6-trichlorophenyl)
 methane, N-trichloromethylmercapto-4-cyclohexene-1,2-dicarbox-
 imide, N-(1,1,2,2-tetrachloroethylsulfenyl)-cis-Δ-4-cyclohexene-
 1,2-dicarboximide, and mixtures thereof.

15. The composition of Claim 13 wherein the particulate substance is a material which improves skin feel when affixed thereto.

16. The composition of Claim 13 wherein the particulate substance is a fabric brightener.


17. The composition of Claim 13 wherein the particulate substance is an ultraviolet absorber.

18. A detergent composition substantially as hereinbefore described.

19. A method for enhancing the deposition and retention of particulate substances upon surfaces washed with a detergent composition, substantially as hereinbefore described.

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